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EXAFS of Germanium Atoms in Germanate Crystals and its Application to Chemical State Analysis of Germanate Glasses
(Commemoration Issue Dedicated to Professor Megumi Tashiro on the Occation of his Retirement)

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CITATION:

Sakka, Sumio ...[et al]. EXAFS of Germanium Atoms in Germanate Crystals and its Application to Chemical State Analysis of Germanate Glasses (Commemoration Issue Dedicated to Professor Megumi Tashiro on the Occation of his Retirement). Bulletin of the Institute for Chemical Research, Kyoto University 1981, 59(3): 172-183

ISSUE DATE:

1981-09-01

URL:

<http://hdl.handle.net/2433/76946>

RIGHT:

EXAFS of Germanium Atoms in Germanate Crystals and its Application to Chemical State Analysis of Germanate Glasses

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Received March 21, 1981

The EXAFS (extended X-ray absorption fine structure) method was applied to the state analysis of the germanium atoms in $\text{Na}_2\text{O}-\text{GeO}_2$ glasses. The validity of the convenient graphical analysis of the EXAFS spectra measured with the conventional X-ray machine was examined using several alkali germanate crystals containing different amounts of the 6-coordinated germanium atoms. It was clearly seen that the spectrum pattern and the value of $R_1-\alpha_1$ related to the Ge-O distance, which was obtained from the intervals between maxima and minima of the spectra, showed the reasonable change with the increase of the amount of the 6-coordinated germanium atoms. The occurrence of the 6-coordinated germanium atoms in the $\text{Na}_2\text{O}-\text{GeO}_2$ glasses was clarified by comparing the EXAFS data of the glasses with those of the germanate crystals.

KEY WORDS: EXAFS/ Alkali germanate crystals/ $\text{Na}_2\text{O}-\text{GeO}_2$ glasses/
Coordination number/ Germanium/

I. INTRODUCTION

The X-ray K edge absorption spectrum of an atom is composed of the Kossel structure within 2 or 3 eV of the edge and the Kronig structure 100~500 eV above the edge. The EXAFS (extended X-ray absorption fine structure), corresponding to the latter, is the oscillating part lying along the smoothly decreasing part on the high energy side of the spectrum. Stern¹⁾ described the EXAFS of an atom in terms of the coordination number of the atom and the distance to the neighbors of the absorbing atom, showing that the EXAFS provides us with the information on the spacial arrangement of the atoms in the immediate vicinity of the absorbing atom.

The advantage of the EXAFS technique over the X-ray diffraction and other spectroscopic methods is that the chemical state of a particular atom in the multicomponent materials can be determined independently from other atoms than the immediate surroundings.

In the present work, the EXAFS technique was applied to the state analysis of the germanium in $\text{Na}_2\text{O}-\text{GeO}_2$ glasses using a conventional X-ray machine and a convenient graphical method of analysis.^{2,3)} For that purpose, the EXAFS spectra of the germanium atoms in alkali germanate crystals with known structures were measured, and the information obtained was applied to the spectra of the glasses to determine the coordination state of the germanium.

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The alkali germanate glasses have attracted much attention of investigators, because the glasses show the so-called germanate anomaly in the property-composition curves.^{4,5)} This anomaly has been explained on the basis of the change in the coordination number of germanium atoms from 4 to 6 on addition of alkali oxide to the GeO_2 glass. The occurrence of the 6-coordinated germanium atoms in the alkali germanate glasses has been revealed by infrared,^{6,7)} Raman spectroscopy⁸⁾ and X-ray diffraction technique.⁹⁾ However, there still remains some uncertainty in the above conclusion. The other atoms than the germanium and immediate neighbors may also contribute to the spectra and the exclusion of such contribution is difficult. It is expected that the EXAFS technique should give supplementary information on the state of germanium in the alkali germanate glasses. So far, the EXAFS spectra of germanium in the GeO_2 crystals, GeO_2 glass,^{2,10,11,12)} and some multicomponent germanosilicate glasses¹⁰⁾ have been reported.

II. EXPERIMENTAL PROCEDURE

1 Preparation of the germanate crystals and glasses

The GeO_2 of the quartz and rutile type and the alkali germanate crystals containing different amounts of 6-coordinated germanium atoms were prepared. The quartz type GeO_2 powder of 7-nine purity supplied by Mitsuwa Chemicals Company and reagent grade sodium and lithium carbonates supplied by Wako Chemicals Company were used as starting materials.

The rutile type GeO_2 containing only 6-coordinated germanium atoms was synthesized by heating the quartz type GeO_2 powder with addition of 0.5 wt % Li_2CO_3 at 950°C for 20 h. The metastable $\text{Na}_2\text{Ge}_4\text{O}_9$ was prepared by cooling the melt of the composition 20 Na_2O -80 GeO_2 in mole at an appropriate cooling rate.¹³⁾ The ratio of 6-coordinated germanium to the total germanium in that crystal is 25%.¹⁴⁾

The thermodynamically stable $\text{Na}_4\text{Ge}_9\text{O}_{20}$ was prepared by heating the glass of the composition 18.2 Na_2O -81.8 GeO_2 in mole at 650°C .¹³⁾ The four germanium atoms among nine, namely 44.4% of germanium are 6-coordinated in the crystal.¹⁵⁾ The 4-coordinated and 6-coordinated germanium atoms in the $\text{Na}_4\text{Ge}_9\text{O}_{20}$ have been found to be replaced by silicon and titanium atoms, respectively.¹⁶⁾ $\text{Na}_4\text{Ge}_{9-x}\text{Si}_x\text{O}_{20}$ ($x=1, 3$ and 4) and $\text{Na}_4\text{Ge}_{9-y}\text{Ti}_y\text{O}_{20}$ ($y=1, 2$ and 3) crystals were prepared by heating the corresponding glasses for 3 h at $600\sim 750^\circ\text{C}$ depending on the composition.

The metastable $\text{Na}_2\text{Ge}_2\text{O}_5$ ¹⁷⁾ was prepared by heating the glass of the composition 33.3 Na_2O -66.7 GeO_2 in mole at 550°C for 10~20 min. Pieces of the glass were put into the furnace held at 550°C and taken out after a period. The stable Na_2GeO_3 crystal was prepared by cooling the melt of the composition 50 Na_2O -50 GeO_2 in mole from 1200°C . Li_4GeO_4 was made by heating the mixture of Li_2CO_3 and GeO_2 corresponding to the composition at 1000°C for 20 h.¹⁸⁾ In the $\text{Na}_2\text{Ge}_2\text{O}_5$, Na_2GeO_3 and Li_4GeO_4 , all the germanium atoms are 4-coordinated. The GeO_4 tetrahedra are linked with each other to form the two-dimensional sheets in $\text{Na}_2\text{Ge}_2\text{O}_5$ and the infinite chains in Na_2GeO_3 , respectively. They are isolated in Li_4GeO_4 .

The ratio of 6-coordinated germanium to the total germanium atoms and the mean shortest distances, Ge-O, in the prepared crystals are listed in Table I. The distances Ge-O in $\text{Na}_4\text{Ge}_{9-x}\text{Si}_x\text{O}_{20}$ and $\text{Na}_4\text{Ge}_{9-y}\text{Ti}_y\text{O}_{20}$ were estimated, assuming that the Ge-O distances in GeO_4 and GeO_6 groups would not differ from those in $\text{Na}_4\text{Ge}_9\text{O}_{20}$.

The glasses of the composition of $x\text{Na}_2\text{O} \cdot (100-x)\text{GeO}_2$ ($x=0, 10, 20$ and 33.3) in mole were prepared by melting the mixture of Na_2CO_3 and quartz type GeO_2 powder in the platinum crucibles at temperatures of $1100 \sim 1500^\circ\text{C}$.

Table I. The amounts of the 6-coordinated germanium atoms and mean Ge-O distances of the germanate crystals

Crystal	Amount of 6-co-ordinated Ge (%)	Mean Ge-O distance (Å)
1 GeO_2 (rutile)	100.0	1.90
2 $\text{Na}_4\text{Ge}_5\text{Si}_4\text{O}_{20}$	80.0	1.86
3 $\text{Na}_4\text{Ge}_6\text{Si}_3\text{O}_{20}$	66.7	1.83
4 $\text{Na}_4\text{Ge}_8\text{SiO}_{20}$	50.0	1.82
5 $\text{Na}_4\text{Ge}_9\text{O}_{20}$	44.4	1.81
6 $\text{Na}_4\text{Ge}_8\text{TiO}_{20}$	37.5	1.80
7 $\text{Na}_4\text{Ge}_7\text{Ti}_2\text{O}_{20}$	28.6	1.79
8 $\text{Na}_2\text{Ge}_4\text{O}_9$	25.0	1.75
9 $\text{Na}_4\text{Ge}_6\text{Ti}_3\text{O}_{20}$	16.7	1.77
10 GeO_2 (quartz)	0.0	1.74
11 $\text{Na}_2\text{Ge}_2\text{O}_5$	0.0	—
12 Na_2GeO_3	0.0	1.76 ²¹⁾
13 Li_4GeO_4	0.0	(1.76~1.77) ²¹⁾

2 EXAFS measurement

The specimen for the EXAFS measurements were prepared as films after White and McKinsty.¹⁰⁾ The crystals or glasses were pulverized to powder under 350 mesh. The solution of 2 : 1 ethylene dichloride-formvar was added to the powder in an agate mortar to form a thin slurry. The ratio of the solution to powder was kept at one to one by volume. The slurry was painted onto a teflon strip one layer at a time with a small brush. The coat was kept standing to dryness before the next layer was brushed on. The film was easily taken apart from the strip and used as the specimen. The uniform thickness of the film was attained by changing the orientation of the brush stroke from coat to coat. The film thickness was kept at less than 0.2 mm.

The conventional X-ray generator and the wide angle goniometer (Rigaku Denki Co., SG-7) equipped with a lithium fluoride crystal as a monochromator were used for the measurements. The schematic diagram of the spectrometer is shown in Fig. 1. The Cu target X-ray tube was used. It was operated at $20 \sim 30$ kV and $10 \sim 25$ mA. The line focusing was made with the 0.5 degree divergence slit, 0.05 mm receiving slit and 0.5 degree scattering slit. The specimen was placed in the incident beam. The scintillation counter was used for intensity measurements.

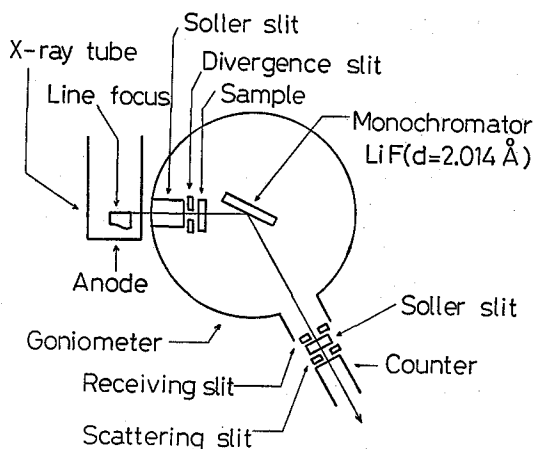


Fig. 1. Diagram of the spectrometer for the EXAFS measurement.

The X-ray intensity measurements were made over one degree in 2θ on the low angle (high energy) side and 0.5 degree on the high angle (low energy) side of the germanium K absorption edge which was at 32.2° in 2θ . The transmitted intensity I was measured at 0.02° interval in 2θ for 40 seconds to accumulate about 10,000 counts. The intensity of the incident beam I_0 was obtained also at 0.02° interval over the same range of 2θ without specimen. The absorption coefficient μx was given by the following equation,

$$\mu x = \ln(I_0/I), \quad \dots\dots\dots(1)$$

where x is the thickness of specimen. The measurement was repeated several times for a sample. Before and after the measurement for a sample, the K-absorption edge of germanium of the quartz type GeO_2 crystal was measured for calibrating the angle 2θ .

3 Analysis of the EXAFS spectra

The EXAFS, $\chi(k)$, originating from the interference between photoelectron wave outgoing from an absorbing atom and that diffracted by the neighbors, is expressed as follows;²⁾

$$\chi(k) = \frac{m}{4\pi\hbar^2 k} \sum_j \frac{N_j}{R_j^2} t_i(2k) e^{-R_j/\lambda} \cdot \sin[2kR_j + 2\delta_j(k)] e^{-2k^2\sigma_j^2}, \quad \dots\dots\dots(2)$$

where m is the electron mass, \hbar is Planck's constant, k is the electron wave vector, N_j is the number of atoms in the j -th coordination sphere, R_j is the average distance from the absorbing atom to the j -th atom, $t_i(2k)$ is the back-scattering matrix element encountered by the electrons, λ is the mean free path of the electron, the second exponential term containing root-mean-square fluctuation σ_j is the Debye-Waller type term and $\sin[2kR_j + 2\delta_j(k)]$ is the interference term, $\delta_j(k)$ being the phase shift. The kinetic energy of the photoelectron ejected from the absorbing atom is:

$$E - E_{\text{edge}} = \hbar^2 \mathbf{k}^2 / 2m. \quad \dots\dots\dots(3)$$

Accordingly, \mathbf{k} is given in reciprocal angstrom as,

$$\mathbf{k} = [0.263(E - E_{\text{edge}})]^{1/2}. \quad \dots\dots\dots(4)$$

The Fourier analysis of Eq. (2) determines the number of atoms in the j -th coordination sphere and the average distance R_j . On the other hand, it has been shown that the distance to the nearest neighbor R_1 and phase shift $\delta_1(\mathbf{k})$ can be determined by a convenient graphical method.^{2,3)} The method is based on the fact that the EXAFS is usually dominated by the scattering from the nearest neighbors. In the present work, the EXAFS of the germanium was analyzed by the convenient graphical method.

The principal maxima and minima in the EXAFS spectrum are determined mainly by the sine term with $j=1$, namely $\sin [2\mathbf{k}R_1 + 2\delta_1(\mathbf{k})]$ in Eq. (2). If the phase shift $\delta_1(\mathbf{k})$ is linear with regard to \mathbf{k} , then $\delta_1 = -\alpha_1 \mathbf{k} + \beta_1$, and the argument of the sine term is $2\mathbf{k}(R_1 - \alpha_1) + 2\beta_1$. The maxima and minima of the EXAFS are given when the following condition is satisfied;

$$(n + 1/2)\pi = 2\mathbf{k}(R_1 - \alpha_1) + 2\beta_1, \quad \dots\dots\dots(5)$$

where n denotes integers. The even numbers $n=0, 2, 4, \dots$ correspond to the maxima and the odd numbers $n=1, 3, 5, \dots$ to the minima, respectively. In Eq. (5), the \mathbf{k} equaling zero corresponds to the E_{edge} . The $R_1 - \alpha_1$ will be determined from the slope of the n vs \mathbf{k} plot for the maxima and minima of the EXAFS divided by $\pi/2$. Since α_1 is believed to be constant determined by the species of the absorbing atom and type of chemical bonding, the distance R_1 is obtained if α_1 is known. When α_1 is difficult to be estimated, it may be possible to relate the change in $R_1 - \alpha_1$ with the change of chemical state of the absorbing atom which is accompanied by the change in the distance R_1 . In the present work, $R_1 - \alpha_1$ is used as a parameter instead of R_1 for the state analysis of germanium.

III. RESULTS

1 EXAFS of the quartz type GeO_2 crystal of different specimen thicknesses

Figure 2 shows the EXAFS spectra of the germanium in the quartz type GeO_2 for different specimen thickness. The spectrum obtained with the thickness less than 0.17 mm as shown in this figure is identical with those^{10,11,12)} reported by other authors. The peak height ratio of the first peak to the second and the intervals between maxima and minima are seen to decrease with an increase of the specimen thickness. It should be noted that the spectrum obtained with the thickness larger than 0.25 mm is similar to that of the rutile type GeO_2 ¹⁰⁾ than to the quartz type GeO_2 . The similar tendency of the change in the spectrum with the specimen thickness was observed for other crystals and glasses. This is the reason why the specimen thickness was kept at less than 0.2 mm. Any serious problems were not encountered in obtaining the EXAFS spectrum with a reasonable reproducibility as far as the specimen less than 0.2 mm in

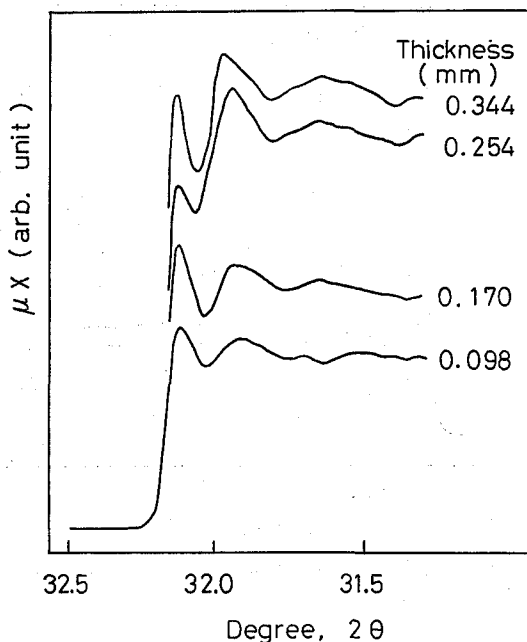


Fig. 2. EXAFS spectra of the quartz type GeO_2 of different specimen thicknesses.

thickness was used, even when the film surface was not smooth or the film had some pinholes.

2 EXAFS of the alkali germanate crystals containing 6-coordinated germanium atoms

The EXAFS spectra of the quartz and rutile type GeO_2 , $\text{Na}_2\text{Ge}_4\text{O}_9$, $\text{Na}_4\text{Ge}_9\text{O}_{20}$, $\text{Na}_4\text{Ge}_{9-x}\text{Si}_x\text{O}_{20}$ ($x=1, 3$ and 4) and $\text{Na}_4\text{Ge}_{9-y}\text{Ti}_y\text{O}_{20}$ ($y=1, 2$ and 3) crystals are shown in Fig. 3. The spectra are arranged in the increasing order of the amount of the 6-coordinated germanium atoms from the bottom to the top. It is seen that the peak height ratio of the first peak to the second is increased and the peak interval is decreased with an increase of the amount of the 6-coordinated germanium atoms.

Examples of the n vs k plot for the crystals are shown in Fig. 4. The first maximum of the spectrum to which n equaling zero corresponds is omitted in n vs k plot, because it has an origin different from the EXAFS. The $R_1 - \alpha_1$ of the crystals are shown in Fig. 5 as a function of the percentage of the 6-coordinated germanium atoms. The bars attached to the circles in the figure indicate the scattering of the $R_1 - \alpha_1$ value in three to five measurements. The values of $R_1 - \alpha_1$ for $\text{Na}_4\text{Ge}_9\text{O}_{20}$ and $\text{Na}_2\text{Ge}_4\text{O}_9$ are plotted at 44.4% and 25.0% for the abscissa, respectively. The values of $R_1 - \alpha_1$ which are plotted on the left hand side of the plot for the $\text{Na}_4\text{Ge}_9\text{O}_{20}$ belong to the $\text{Na}_4\text{Ge}_{9-y}\text{Ti}_y\text{O}_{20}$ crystals except one plotted at 25.0%. The data on the right hand side of the plot for the $\text{Na}_4\text{Ge}_9\text{O}_{20}$ belong to the $\text{Na}_4\text{Ge}_{9-x}\text{Si}_x\text{O}_{20}$ crystals. It is seen that the $R_1 - \alpha_1$ increases with increasing percentage of the 6-coordinated germanium atoms, although the scattering is pretty large. It is especially noticeable that the

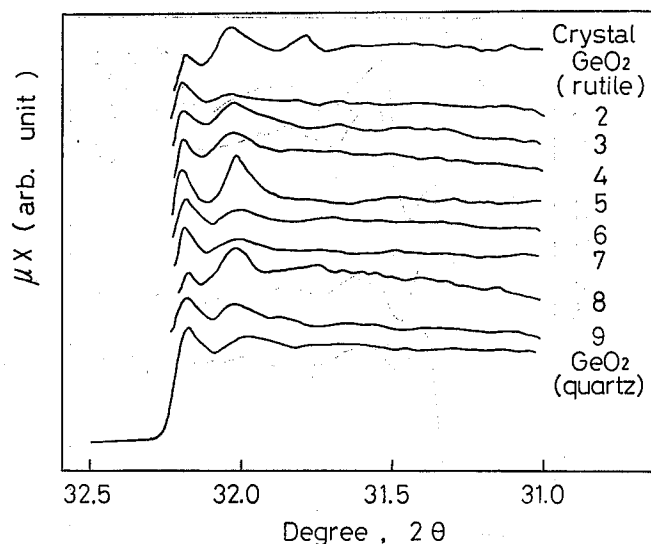


Fig. 3. EXAFS spectra of the alkali germanate crystals containing 6-coordinated germanium atoms.

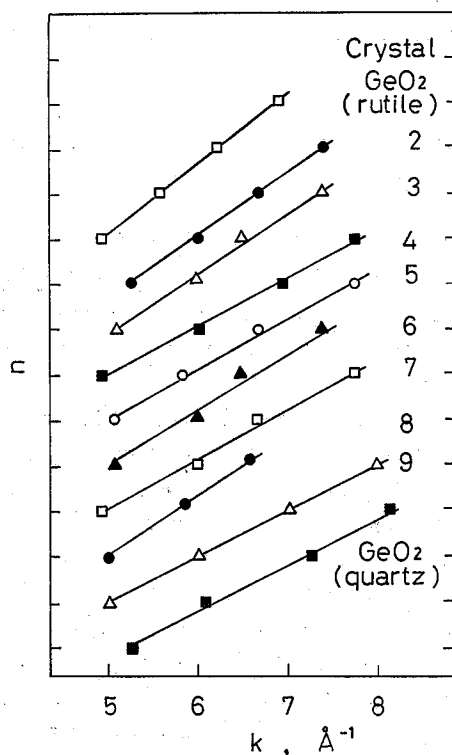


Fig. 4. The n vs k plots for the germanate crystals containing 6-coordinated germanium atoms.

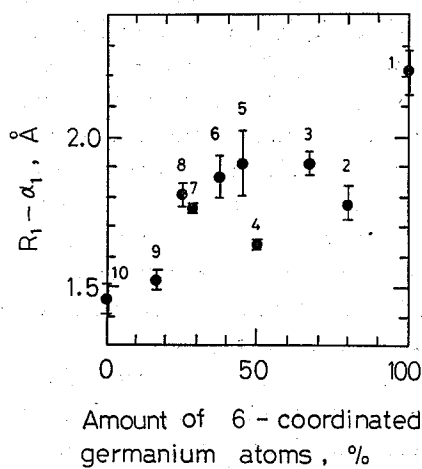


Fig. 5. Change of the $R_1 - \alpha_1$ with the amount of the 6-coordinated germanium atoms. The numbers attached to the circles are sample numbers shown in Table I.

values of $R_1 - \alpha_1$ for the $\text{Na}_4\text{Ge}_{9-x}\text{Si}_x\text{O}_{20}$ are smaller than expected from those for $\text{Na}_4\text{Ge}_9\text{O}_{20}$, $\text{Na}_4\text{Ge}_{9-y}\text{Ti}_y\text{O}_{20}$ and $\text{Na}_2\text{Ge}_4\text{O}_9$ crystals.

3 Spectra of the alkali germanate crystals in which all the germanium atoms are 4-coordinated

The EXAFS spectra of $\text{Na}_2\text{Ge}_2\text{O}_5$, Na_2GeO_3 and Li_4GeO_4 are shown in Fig. 6 together with those of the quartz and rutile type GeO_2 . The patterns of the spectra of three alkali germanate crystals are similar to the quartz type GeO_2 . The $R_1 - \alpha_1$ of the crystal is plotted in Fig. 7 against the amount of the alkali oxide content. It is seen that the $R_1 - \alpha_1$ increases as the alkali oxide content increases. It should be

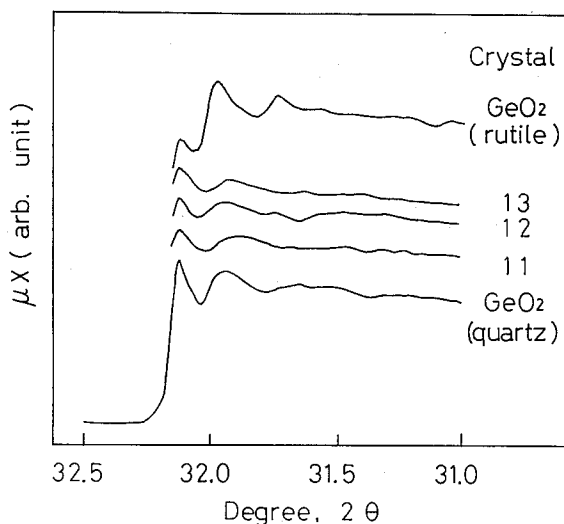


Fig. 6. EXAFS spectra of the alkali germanate crystals in which all the germanium atoms are 4-coordinated.

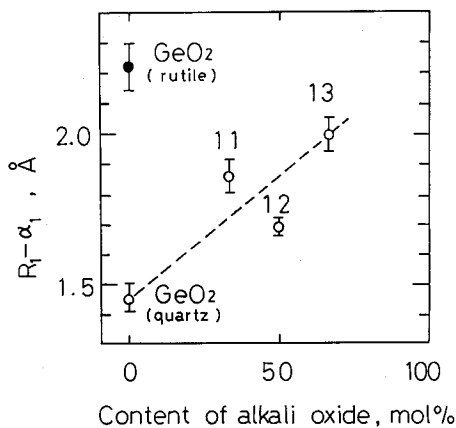


Fig. 7. Change of the $R_1 - \alpha_1$ with the content of alkali oxide for the crystals in which all the germanium atoms are 4-coordinated. The numbers attached to the circles are sample numbers shown in Table I.

noted that the increase of the $R_1-\alpha_1$ relative to the quartz type GeO_2 occurs even for the alkali germanate crystals in which all the germanium atoms are 4-coordinated. In the three germanates, the GeO_4 groups are linked with each other in different modes and the number of non-bridging oxygen atoms is different. It is assumed that the content of non-bridging oxygens corresponds to the increase of the alkali oxide content. Therefore it can be said that the $R_1-\alpha_1$ of the crystal increases with the increase of non-bridging oxygens.

4 Spectra of the $\text{Na}_2\text{O}-\text{GeO}_2$ glasses

The EXAFS spectra of the $\text{Na}_2\text{O}-\text{GeO}_2$ glasses are shown in Fig. 8. It is seen that the pattern of the spectrum and the $R_1-\alpha_1$ of the GeO_2 glass is almost identical

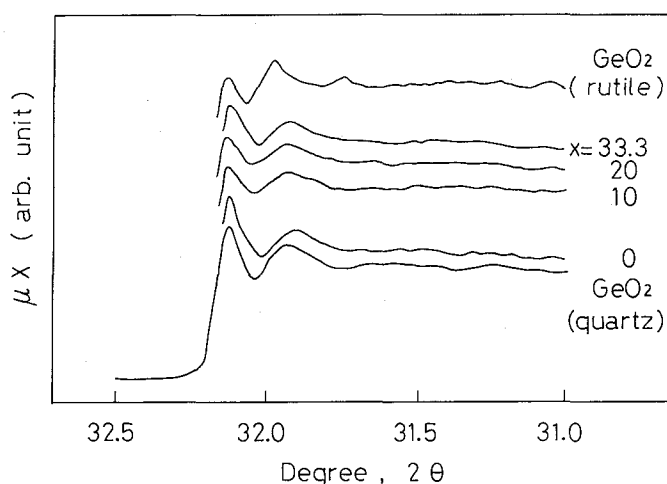


Fig. 8. EXAFS spectra of the $x\text{Na}_2\text{O} \cdot (100-x)\text{GeO}_2$ glasses.

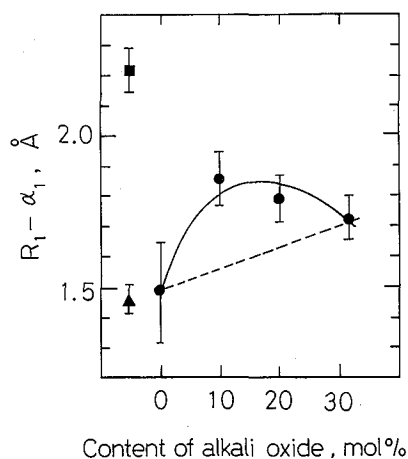


Fig. 9. Change of the $R_1-\alpha_1$ with the content of the alkali oxide (solid line). The broken line shows the hypothetical change of $R_1-\alpha_1$ with the alkali oxide content obtained for the crystals.

▲; quartz type GeO_2 , ■; rutile type GeO_2

with the quartz type GeO_2 crystal. The $R_1 - \alpha_1$ is shown in Fig. 9 as a function of the Na_2O content. It is seen that the $R_1 - \alpha_1$ increases with the Na_2O content, showing a maximum at 10~20 mol % Na_2O .

IV. DISCUSSION

1 Validity of the graphical method for the state analysis of germanium

The phase shift $\delta_j(\mathbf{k})$ in the Eq. (2) was assumed to be linear with regard to \mathbf{k} . Lytle *et al.*²⁾ showed that in the case of GeO_2 the phase shift could not be approximated by linear dependence on \mathbf{k} . The non-linear dependence gave rise to the additional peaks at shorter interatomic distances than 1.42 Å in the radial distribution curve obtained by Fourier analysis. The n vs \mathbf{k} plots made in the present work over the small range of the photoelectron energy, however, showed the linear relationship for all the crystals examined. Furthermore, the $R_1 - \alpha_1$ of the quartz type GeO_2 was 1.45 Å, agreeing with the distance of 1.42 Å obtained by Lytle *et al.* with the use of Fourier analysis.²⁾ These facts indicate that the phase shift in the GeO_2 has a linear dependence on \mathbf{k} in the limited range of the photoelectron energy and the convenient graphical method is still valid for determining the state of the germanium atoms.

It has been shown that the α_1 is determined by the species of the X-ray absorbing atom and the type of chemical bonding to the neighbors. The α_1 determined for the quartz type GeO_2 in the present work was 0.29 Å, agreeing fairly well with 0.25~0.27 Å of the germanium for covalent structures. The $R_1 - \alpha_1$ for the rutile type GeO_2 was 2.22 Å and even larger than the distance Ge-O of the crystal. The α_1 estimated was -0.32 Å and was considerably different from that of the quartz type GeO_2 . This may be caused by the fact that the bonding state of the germanium to the neighbors might differ from the covalent state. The distance from the absorbing germanium to the nearest germanium atoms in the rutile type GeO_2 is 2.66 Å and does not differ so much from the distance to the oxygen atoms of 1.90 Å. The maxima and minima due to the backscattering of the photoelectron from the nearest germanium, then, might overlap on the major maxima and minima due to the oxygen atoms, giving a large $R_1 - \alpha_1$ compared to 1.90 Å of the real crystal.

It is clear from the examination of the EXAFS of the germanate crystals (Figs. 3 and 5) that the increase of the percentage of the 6-coordinated germanium atoms which accompanies the increase of the mean distance Ge-O is reflected on the pattern of the spectrum and the decrease of the intervals between maxima and minima. The values of $R_1 - \alpha_1$ of the $\text{Na}_4\text{Ge}_{9-x}\text{Si}_x\text{O}_{20}$ in Fig. 5 were slightly smaller than expected from $\text{Na}_4\text{Ge}_{9-y}\text{Ti}_y\text{O}_{20}$, $\text{Na}_2\text{Ge}_4\text{O}_9$ and $\text{Na}_4\text{Ge}_9\text{O}_{20}$. This may be due to the smaller distances than those estimated, assuming that the Ge-O distances of the GeO_4 and GeO_6 groups in the $\text{Na}_4\text{Ge}_9\text{O}_{20}$ would not change even when some germanium atoms were replaced by the silicon atoms. It is, then, concluded that detecting the presence of the 6-coordinated germanium atoms and predicting its amount in the material is possible by analyzing the EXAFS spectra by the convenient graphical method instead of the Fourier analysis method.

It should be remarked that the $R_1-\alpha_1$ obtained by the convenient method is naturally changed when the coordination state of the absorbing germanium atom is varied and also affected by the mode of linkage of the GeO_4 groups or alkali oxide content of the crystal as seen in Fig. 7. These two contributions to the $R_1-\alpha_1$ have to be taken into account when the EXAFS data on crystals are applied to the $\text{Na}_2\text{O-GeO}_2$ glasses.

2 Chemical state of the germanium atoms of the $\text{Na}_2\text{O-GeO}_2$ glasses

It was found that the values of $R_1-\alpha_1$ of the $\text{Na}_2\text{O-GeO}_2$ glasses are larger than that of the quartz type GeO_2 . Recently, Nukui *et al.*²⁰⁾ analyzed the EXAFS spectra of the $\text{Na}_2\text{O-GeO}_2$ glasses using the Fourier transformation method, showing that the distance Ge-O increased on the addition of Na_2O to the GeO_2 glass. These indicate that some part of the germanium atoms in the glasses are 6-coordinated with oxygen atoms. Nukui *et al.*²⁰⁾ did not mention the content of the 6-coordinated germanium atoms quantitatively. To estimate the content of the 6-coordinated germanium atoms from the $R_1-\alpha_1$ of the glass, the two different contributions to the $R_1-\alpha_1$ have to be taken into account as shown for the crystals. The hypothetical contribution of the remaining GeO_4 group to the $R_1-\alpha_1$ of the glass is given by a broken line in Fig. 9 which is obtained from the data on crystals. The net change of the $R_1-\alpha_1$ due to the 6-coordinated germanium is then given by the difference between the solid and broken lines. The maximum content of the 6-coordinated germanium atoms of about 40% results at 10~20 mol %, being a little larger than those derived from infrared spectroscopy⁷⁾ and X-ray diffraction.⁹⁾

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